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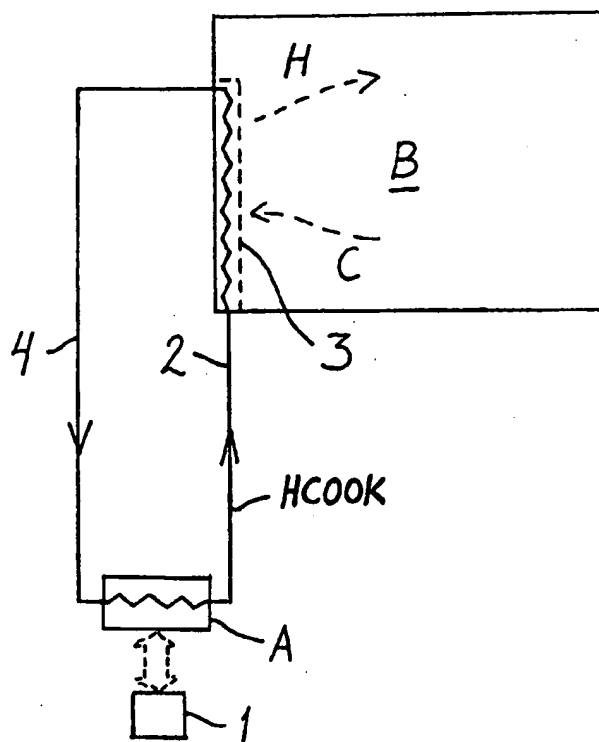
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(21) International Application Number: PCT/FI96/00327 (22) International Filing Date: 31 May 1996 (31.05.96)  (30) Priority Data: 952760 6 June 1995 (06.06.95) FI 955754 29 November 1995 (29.11.95) FI  (71) Applicant (for all designated States except US): KEMIRA CHEMICALS OY [FI/FI]; Porkkalankatu 3, FIN-00180 Helsinki (FI).  (72) Inventors; and (75) Inventors/Applicants (for US only): AITTA, Eero [FI/FI]; Lottakuja 11, FIN-91410 Jokirinne (FI). VARILA, Elias [FI/FI]; Kerrostie 8 B, FIN-90940 Jääli (FI). VAPAAOKSA, Pekka [FI/FI]; Ristinarkuntie 3 C, FIN-33700 Tampere (FI).  (74) Agents: HAKOLA, Unto et al.; Tampereen Patenttitoimisto Oy, Kanslerinkatu 6, FIN-33720 Tampere (FI).			(81) Designated States: CA, JP, NO, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report. In English translation (filed in Finnish).

(54) Title: A METHOD FOR PERFORMING HEAT EXCHANGE BY USING A HEAT TRANSFER MEDIUM, A HEAT TRANSFER MEDIUM AND A HEAT EXCHANGE APPARATUS

(57) Abstract

For performing heat exchange with a target (B) by using a heat transfer medium so that heat transfer takes place as the medium moves relative to the target (B) simultaneously undergoing mixing aqueous solution of potassium formate is used as the medium. The heat transfer medium is either a cooling medium for cooling (C) the target (B) or heating medium for heating (H) the target (B).



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A method for performing heat exchange by using a heat transfer medium, a heat transfer medium and a heat exchange apparatus

- 5     The invention relates to a method for performing heat exchange by using a heat transfer medium wherein heating takes place by heat exchange from the target to the medium or from the medium to the target. The invention also relates to a medium and a heat exchange apparatus.
- 10     Particularly at low operating temperatures a cooling medium for cooling a target is used as far as possible so that the medium does not solidify at any stage of the process nor do any of its dissolved components crystallize.
- 15     A cooling medium should consequently remain in liquid form at its operating temperatures. In indirect cooling the cooling medium is cooled to its lowest temperature after which it is brought into heat transfer contact with the target to be cooled which then cools by
- 20     releasing heat to the cooling medium. Heat transfer is also influenced by the viscosity of the medium.
- 25     Besides the cooling media also the heating media belong to heat transfer media. Similar properties are required from them as the cooling media since in both cases efficient heat transfer is important between the target and the medium regardless of the direction. Particularly in spaces which are temporarily heated the heating medium should also stand low temperatures.
- 30     Temporarily heated spaces include caravans, boats, touring vehicles, summer cottages, temporarily heated sheds and storehouses of various kinds, and small transferable houses like rest cabins which are not meant for continuous living. Heating of such inside spaces is problematic because direct heating means like e.g. electricity is not
- 35     always available.

When gas, oil, wood, or petrol oil is used in direct heating a voluminous heating apparatus is required and furthermore the fire safety may be

endangered. Therefore, indirect radiator heating has become more common in heating e.g. caravans wherein the heating apparatus, e.g. a gas burner may be placed outside the space to be heated and a heating fluid, normally aqueous solution of ethylene glycol, circulates in the radiators.

This kind of indirect heating system has proved safe and relatively efficient. Its drawback is that instead of water one has to use the aforementioned aqueous solution of ethylene glycol or other heat transfer medium which have low heat transfer capacity and hence heating takes place slowly and high pumping power is needed to move the solution. In most cases, however, only a battery or an accumulator is available as the power source.

Besides pumping power the heat transfer capacity of the solution has an essential influence on the heating efficiency. The best heat transfer capacity can be obtained with water. ~~The drawback with water is that it~~ can cause serious damage to the apparatus in spaces which temporarily cool below zero. Ethylene glycol does not have this drawback but the heat transfer capacity of ethylene glycol is low due to high viscosity. Due to the surface tension of the ethylene glycol solution it tends to cause leaks e.g. as gaskets deteriorate because of large temperature variations. Leaks in turn are injurious due to the toxicity of ethylene glycol.

In order to replace dangerous ethylene glycol with water based media with various dissolved salts added to depress the freezing point have been commonly used. E.g. the US patent 5104562 discloses a refrigerant with an optimum composition of 1 mole of potassium formate per 6 moles of sodium acetate dissolved in water. According to the US patent 5104562 it would be possible, in the case of pure potassium formate, to reach a freezing point of  $-35^{\circ}\text{C}$  with the salt/water mole ratio of 1:4,72 but even as low as  $-70^{\circ}\text{C}$  with the acetate/formate mole ratio of 6:1.

It is, however, obvious that the measurements in question have been performed by using methods which determine the freezing point without taking into account the effect of mixing of the solution. It has now been

observed that if the refrigerant is set into motion, its freezing properties and hence the cooling properties change completely.

5 It has been observed that, if a cooled liquid in a concentrated solution is mixed, the acetate containing solution crystallizes instantaneously and its pumping properties change essentially.

10 Cooling liquids are often used in conditions where they are motionless for long periods of time so that the solution according to the above mentioned US patent remains unsolidified, but it will solidify when it is set in motion due to vibration, mixing, or pumping.

15 The object of the invention is to obtain a method wherein heat transfer can be realized in an efficient and non-toxic manner. To obtain this object the medium is an aqueous solution of potassium formate.

20 For example, as distinct from the data of the above US patent, potassium formate has excellent properties considering its use as a cooling medium. The method employed in a cooling process is primarily characterized in that the cooling medium is an aqueous solution of potassium formate wherein the number of moles of dissolved components of potassium formate is at least 80 % of the number of moles of all the dissolved components which depress the freezing point of water and mixing takes place in the cooling medium as  
25 it moves relative to the target to be cooled.

Low operating temperatures can be obtained by using potassium formate in sufficiently high concentrations, preferably in a concentration of at least 30 % by weight.

30 The behaviour of a concentrated solution is of great importance since as time goes on the solution may concentrate due to evaporation of water and thereby cause blockages in the pipes of the cooling system. On the other hand, in such indirect cooling systems whose operating  
35 range is at very low temperatures like below - 40 °C, one in any case has to use fairly concentrated solutions and therefore one obtains better reliability due to higher solubility and lower freezing point with potassium formate than acetate also at very low temperatures.

Concentrated potassium formate has also a lower viscosity than potassium acetate.

5 The object of the invention is also to present a heating method, heating medium and heating apparatus which are particularly suitable for nordic winter conditions where the temperature of a temporarily heated space may during the intermediate periods decrease at its lowest even 30 °C below the freezing point of water.

10 The advantages of the invention are obtained by using an aqueous solution of potassium formate as the heat transfer medium. The eutectic point of the known ethylene glycol is at ca -50 °C and then the concentration is nearly 100 percent ethylene glycol. The solution according to the invention has the eutectic point at -70 °C and then the  
15 concentration is 68 % potassium formate. It is from this fact that a solution that stands even extreme cold is a solution containing about 20 -15 % potassium formate. The solution can be manufactured for a given region according to the expected minimum temperatures , and its concentration can be at least 20 % by weight, at least 30 % by weight,  
20 or for the North-European conditions even 50 % by weight or more potassium formate.

Freezing of water divides the solution into two phases, the frozen part and the liquid phase, which prevents damages due to freezing and the  
25 sodium formate solution can be taken into heating use with much less pumping energy than using e.g. ethylene glycol as the solution.

If it is required that the solution be operable at northern winter conditions , the solution of the invention is the best of the known  
30 solutions in terms of its heat transfer properties. Some other salt solutions (e.g. calcium chloride) give nearly equally good results but the corrosion properties are much more difficult to deal with than the solutions of the invention. It has been experimentally observed that 90 % of the heat transfer capacity can be explained by the viscosity of the  
35 corresponding aqueous solution so that also from this point of view the solution of the invention is the best as will be shown later in the presented viscosity comparison in which viscosities of different solutions are compared as a function of the operating temperature. The

operating temperature denotes the temperature 10 °C above the freezing point of the corresponding solution.

5 The invention and the experiments which led thereto will be described in greater detail in the following referring to the enclosed drawings in which

Fig. 1 shows schematically use of a heat transfer medium,

10 Fig. 2 shows the phase diagram of aqueous solution of potassium formate,

Fig. 3 shows the viscosity of aqueous solution of potassium formate at different concentrations as a function of  
15 temperature, and

Fig. 4 shows the viscosity of potassium formate as a function of operating temperature compared with other media.

20 Fig. 1 shows the principles in the use of a heat transfer medium. The question is about a two-stage method in simplified terms. At the starting point A heat transfers between the medium and a heat transfer apparatus 1 which requires external energy. Then the medium is pumped through a conduit 2 to the target B in which heat transfers  
25 between the target B and the medium through a heat transfer surface 3 in a direction reverse of that at the starting point A. The target B is in general a space of a specific size where the medium flows as a flow separated from the space by a heat transfer surface 3 such as cooling pipe system, heating radiator, or the like. From the target B the medium  
30 returns to point A through a conduit 4. It is clear that in case of a cooling medium the apparatus 1 cools the medium and in the case of a heating medium it is heated. Heat transfer in the target B is further indicated by dashed arrows (C = cooling of the space, H = heating of the space). In both cases the medium undergoes heavy mixing as it moves relative to  
35 the target B and there are no phase changes, i.e. the composition of the liquid remains the same.

**EXAMPLE 1: COOLING LIQUID**

- Freezing point of the solution was measured in the following way. The tested solution was dosed in a ( ca. 15 ml) test tube provided with a top. Before closing a glass sphere with a diameter of 8 mm was also placed into the test tube. The test tube ( ca. 30 pieces) was placed on a rack which was immersed in the cooling bath of a cryogenic apparatus. The temperature of the cooling liquid was lowered 5 °C / day from the temperature of 0 °C down to -60 °C. The test tube was checked daily by lifting each tube from the cold bath, inclining the tube so that the glass sphere moved to and fro in the tube producing a mixing motion. Formation of ice crystals was observed visually.
- Formate and acetate solutions according to Table 1 were prepared for the freezing tests. The solutions were prepared by mixing stoichiometric amounts of formic acid / acetic acid and potassium hydroxide.



Table 1. Freezing point tests as well as kinematic viscosities of solutions measured at room temperature.

Test	K-formate %	K-acetate %	Water %	Freezing point °C	Viscosity cSt (20°C)	Remarks
1	60	-	40	-55	2,57	K-formate solution
2	50	-	50	-40	1,91	"
3	40	-	60	-25	1,46	"
4	30	-	70	-15	1,32	"
5	50	10	40	-60	-	K-form/K-acet=5/1
6	41,7	8,3	50	-40	1,94	"
7	33,3	6,7	60	-25	-	"
8	25,0	5	70	-15	-	"
9	40	20	40	-40	-	K-form/K-acet=4/2
10	33,3	16,7	50	-40	2,19	"
11	26,7	13,3	60	-25	-	"
12	20	10	70	-15	-	"
13	30	30	40	-40	-	K-form/K-acet=1/1
14	25	25	50	-45	2,43	"
15	20	20	60	-25	-	"
16	15	15	70	-15	-	"
17	20	40	40	crystall.	-	K-form/K-acet=2/4
18	16,7	33,3	50	-40	2,77	"
19	13,3	26,7	60	-25	-	"
20	10	20	70	-15	-	"
21	10	50	40	crystall.	-	K-form/K-acet=1/5
22	8,3	41,7	50	-35	2,98	"
23	6,7	33,3	60	-35	-	"
24	5,0	25	70	-20	-	"

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The results show that it was possible to obtain lower freezing point with solutions which contained much K-formate (tests 1 and 5) than with much K-acetate containing solutions of equal concentration. Crystallization took place in concentrated K-acetate solutions immediately after the solution was set to motion with the glass sphere.

10

Before the rapid crystallization the solution was completely transparent. After crystallization the solution changed turbid and very solid.

5 Fig. 2 shows the phase diagram of potassium formate in which the freezing point curve is a polynomial fit to the freezing points of potassium formate solutions of various concentrations measured by the applicant and the solubility curve is a polynomial fit to solubility data obtained from literature. At the eutectic point the concentration of potassium formate is 68 % by weight and the freezing point is ca -70°C.

10

Results also show that concentrated K-formate solutions have a clearly lower viscosity (50 % K-formate solution, 1.91 cSt, test 2) than the corresponding K-acetate solutions (50 % K-acetate/K-formate solution, 2.98 cSt, test 22). This is quite significant from the point of view of the pumpability of the coolant. Fig. 3 shows the viscosity of potassium formate of different concentrations as a function of temperature measured with an Ostwald capillary viscosimeter tube held in the cold bath, and Fig. 4 shows the dependence of viscosity of potassium formate and known coolants on operating temperature. Operating temperature, in this case, is a temperature 10 °C above the freezing point of the liquid being used i.e. in one wants to use a cooling medium at -15 °C, he selects solution which has the freezing point at -25 °C, in case of potassium formate a solution with a concentration of ca 35 % by weight whose viscosity at the operating temperature is ca. 4,2 mPas.

15 20 25 30 The figure shows that the viscosity of potassium formate is below those of known cooling media and the difference becomes larger towards lower operating temperatures. The pH-values of the potassium formate solutions are also in a range that requires no special materials in the pipe system. The pH-values of the solutions with 35 and 50 % by weight are 6,17 and 6,71, respectively.

In terms of the properties potassium formate as such is the best alternative for a cooling medium. The freezing point of potassium formate could not be depressed by any additive the applicant tested including potassium acetate, sodium formate, sodium acetate, ethylene glycol, ethanol, urea, and calcium chloride. If other ingredients are mixed with the potassium formate coolant, the number of moles of dissolved components of potassium formate must constitute at least 80

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% of the total number of moles of the dissolved components which depress the freezing point. These dissolved components may be ions or undissociated molecules.

- 5 The following Table 2 shows the effect of some of the above mentioned additives on the freezing point of potassium formate solutions.

10 Table 2. Effect of different additives on the freezing point of the aqueous solution of K-formate at three different concentrations of the solution. The amount of each additive is 20 % of that of K-formate.

K-formate solution + additive	Concentration of the solution		
	20 %	35 %	50 %
K-form (pure solution)	-10 °C	-25 °C	-50 °C
K-form + K-acetate	-15 °C	-25 °C	-50 °C
K-form + Na-formate	-10 °C	-20 °C	-50 °C
K-form + Na-acetate	-15 °C	-25 °C	-50 °C
K-form + Ethyl.glycol	-15 °C	-20 °C	crystallized
K-form + Ethanol	-10 °C	-20 °C	crystallized

#### EXAMPLE 2: HEATING MEDIUM

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A caravan, model Solifer, whose length was 5 m and heated volume about 20 m<sup>3</sup>, was brought into use for the test. To this caravan a gas operated Primus-type heater was installed, which was kept in a box outside the caravan, and inside the caravan 8 m long series of radiators, pump and thermostat were installed.

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25 As the heating solution an ethylene glycol solution with a concentration of 30 % of ethylene glycol was used according to the directions provided by the supplier of the apparatus. A solution which had the same concentration as the ethylene glycol solution and which thereby had lower resistance to freezing than the ethylene glycol was used as the test solution. Another solution was a 20 % potassium formate

solution which was expected to stand -15 °C operating temperature and temporarily even lower temperatures.

Results are shown in the following Table 1.

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Table 1. Comparison of the heating properties of ethylene glycol (EG) and potassium formate.

	Eth. Glyc.	Potassium formate 1	Potassium formate 2
Concentration w-%	30	30	20
+20 viscosity cSt	3,0	1,8	1,4
-10 viscosity cSt	8,9	2,6	2,1
Heat needed kW	6,3	3,3	3,1
Heat transferred W/m <sup>2</sup>	220	400	410

- 10 When using potassium formate the same result can be obtained with a radiator surface area which is about 55 % of that needed with ethylene glycol. It can be further seen that energy requirement drops more than 40 % compared to ethylene glycol when using the concentrated potassium formate solution. When using the dilute solution the needed heating energy drops further.
- 15

Due to the weather conditions during the testing period measurements could not be performed at extreme conditions. Results showed, however, that the colder the weather the more advantageous is the solution of the invention as a heat transfer medium.

20

Besides potassium formate the heat transfer medium may also contain other components which are appropriate for the use of the medium but potassium formate is always the main component constituting over 50 % by weight, preferably over 70 % by weight of all the dissolved components. The other components may be e.g. corrosion inhibitors.

25

The solution used in the method of the invention is easier to manufacture since no harmful acetate is needed and in this respect also the manufacturing costs are lower. Potassium formate used in the invention may be prepared by direct synthesis from carbon dioxide and

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potassium hydroxide in the presence of a suitable catalyst. Potassium acetate cannot be prepared by direct synthesis and thus it is much more expensive than potassium formate manufactured as mentioned above. So it seems obvious that potassium formate made by direct synthesis from carbon monoxide and potassium hydroxide is a useful cooling medium which suits to heat transfer in most applications in which the solution must remain unfrozen down to -40 °C. It is also to be noted that potassium formate has considerably better heat transfer properties than the currently used ethylene glycol. Furthermore, contrary to ethylene glycol, potassium formate is less toxic and the decomposition products are not harmful to nature. Consequently, potassium formate is also well suited to a heating medium and due to its resistance to freezing particularly for use in the heating systems of temporarily heated spaces.

Possible corrosion problems may be prevented by adding suitable inhibitors.

The invention may be used in many existing cooling systems and generally in applications requiring low temperatures and respectively in many existing heating systems.

Furthermore, higher boiling points of potassium formate solutions compared to ethylene glycol may in some situations be an advantage (elevation of the boiling point of water due to dissolved salt). Advantages may show up particularly in case of malfunction and in heating applications where a high temperature heat source is used.

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Claims:

1. Method for performing heat exchange with a target (B) by using a heat transfer medium in which heat transfer takes place as the medium moves relative to the target (B) simultaneously undergoing mixing, characterized in that the medium is an aqueous solution of potassium formate.
2. Method according to claim 1, characterized in that the heat transfer medium is a cooling medium for cooling the target (B) wherein the number of moles of dissolved components of potassium formate is at least 80 % of the number of moles of all the dissolved components depressing the freezing point of water.
3. Method according to claim 2, characterized in that the number of moles of dissolved components formed by potassium formate is at least 90 % of the total number of moles.
4. Method according to claim 2 or 3, characterized in that the concentration of potassium formate in solution is at least 30 % by weight, preferably between 40 % and 65 % by weight.
5. Method according to claim 4, characterized in that potassium formate constitutes at least 98 % by weight of the amount of components dissolved in water the rest being additives like corrosion inhibitors.
6. Method according to any of the above claims, characterized in that potassium formate solution is used at least in some part of the cooling process at a temperature of below -20°C.
7. Method according to claim 6, characterized in that the operating temperature is at least in some part of the cooling process below -30°C, preferably below -40°C.
8. Method according to claim 1, characterized in that the heat transfer medium is a heating medium for heating the target (B) wherein the

portion of potassium formate is over 50 % by weight, preferably over 70 % by weight of all the dissolved ingredients.

5 9. Method according to claim 8, characterized in that it is used for heating temporarily heated spaces where heating is performed by indirect heating by using a heated heating medium.

10 10. Method according to claim 8 or 9, characterized in that the concentration of potassium formate in solution is at least 20 % by weight.

15 11. Method according to claim 9, characterized in that for very low temperatures between the heating periods the concentration of potassium formate in solution is at least 30 % by weight.

12. Pumpable heat transfer medium for performing heat transfer with a target (B), characterized in that it contains potassium formate dissolved in water.

20 13. Heat transfer medium according to claim 12, characterized in that it is a cooling medium containing potassium formate dissolved in water in such an amount that the number of moles of dissolved components of potassium formate is at least 80 % of the number of moles of all the dissolved components depressing the freezing point of water.

25 14. Heat transfer medium according to claim 13, characterized in that the concentration of potassium formate in solution is at least 30 % by weight, preferably 40-65 % by weight.

30 15. Heat transfer medium according to claim 12, characterized in that it is a heating medium in which the portion of potassium formate is over 50 % by weight, preferably over 70 % by weight of all the dissolved ingredients.

35 16. Heat transfer medium according to claim 15, characterized in that the concentration of potassium formate in solution is at least 20 % by weight.

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17. Heat transfer medium according to claim 15, characterized in that for very low temperatures between the heating periods the concentration of potassium formate in solution is at least 30 % by weight.

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18. Heat exchange apparatus comprising a heat transfer unit (1), conduit (2) for pumping the heat transfer medium from the starting point (A) to the target (B) and heat transfer surface (3) for performing heat transfer (C,H) between the target (B) and the medium, characterized in

10

that the apparatus comprises a medium according to any of the above claims 12-17 as the heat transfer medium.

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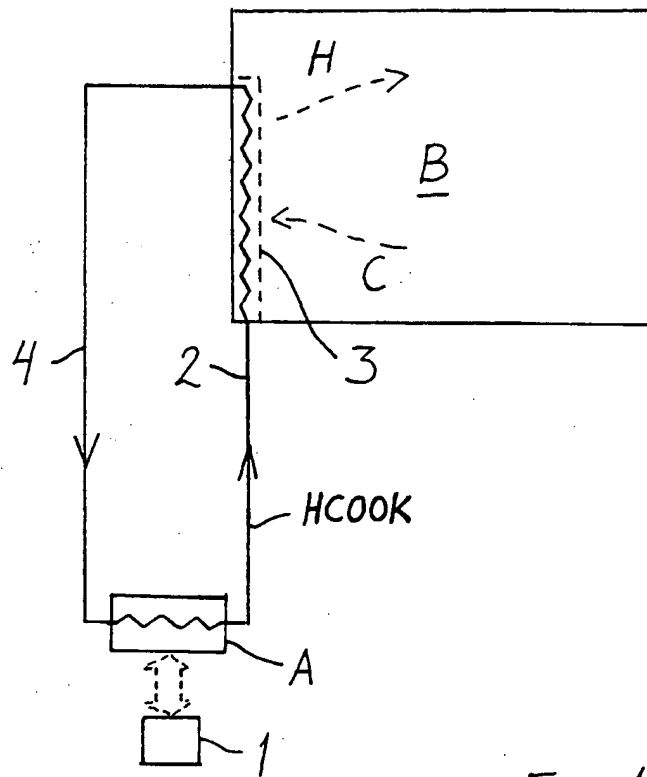
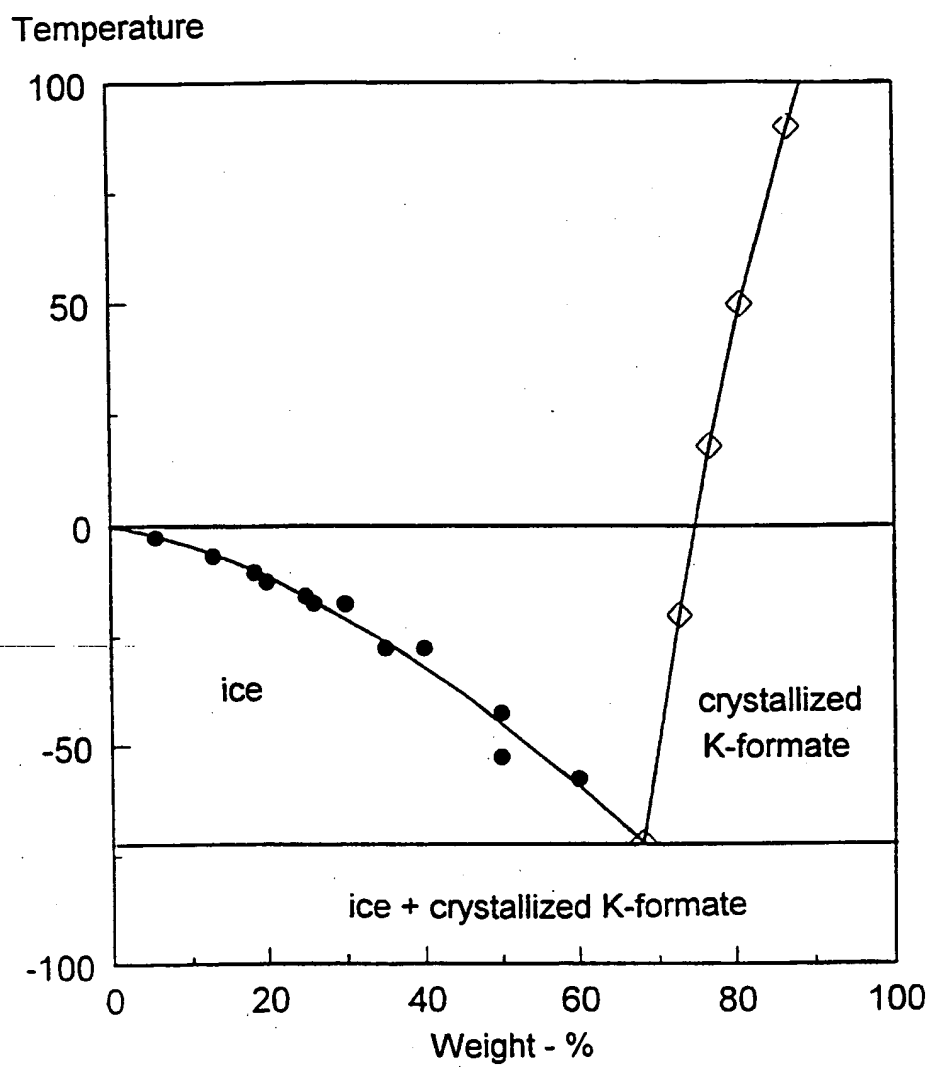
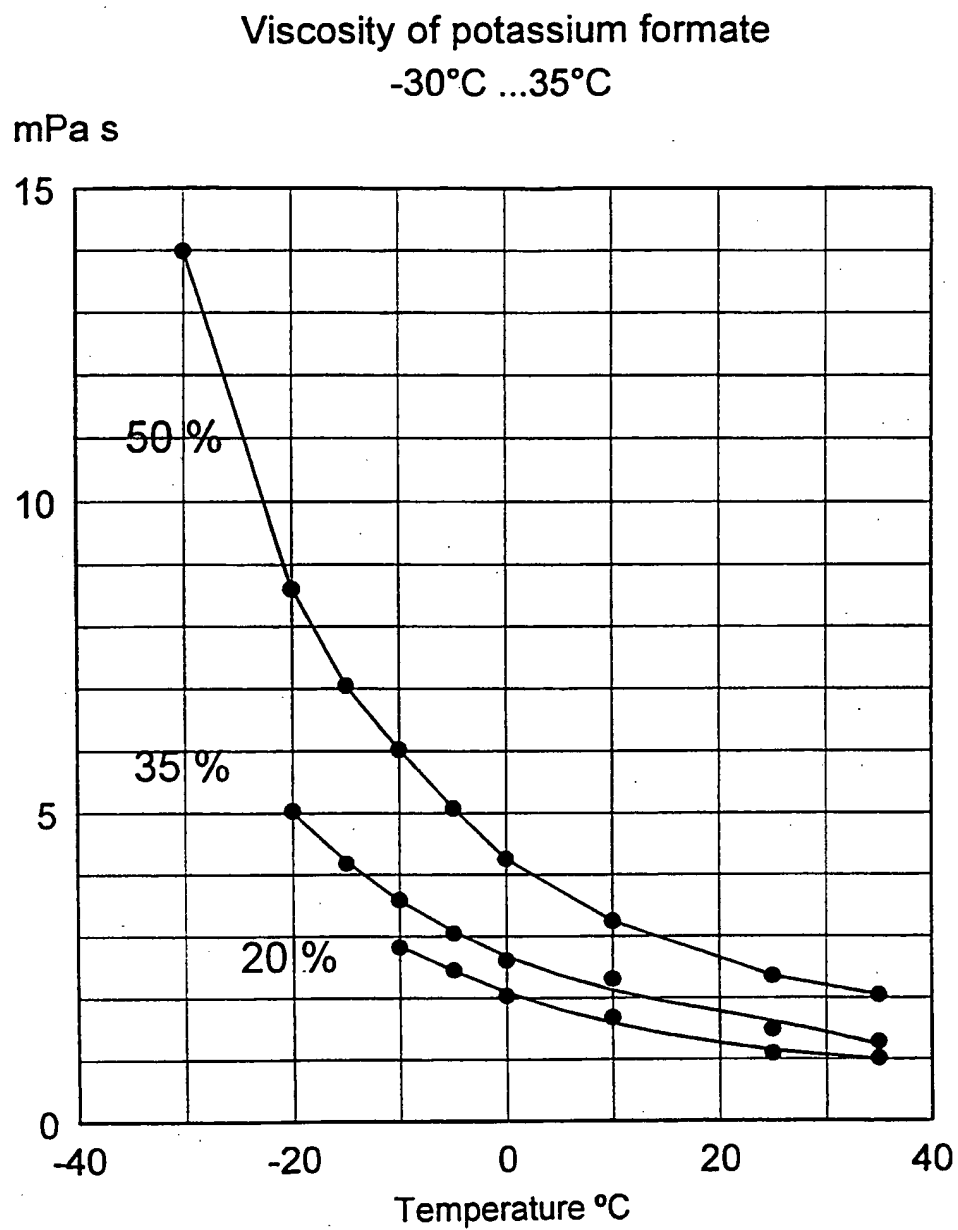
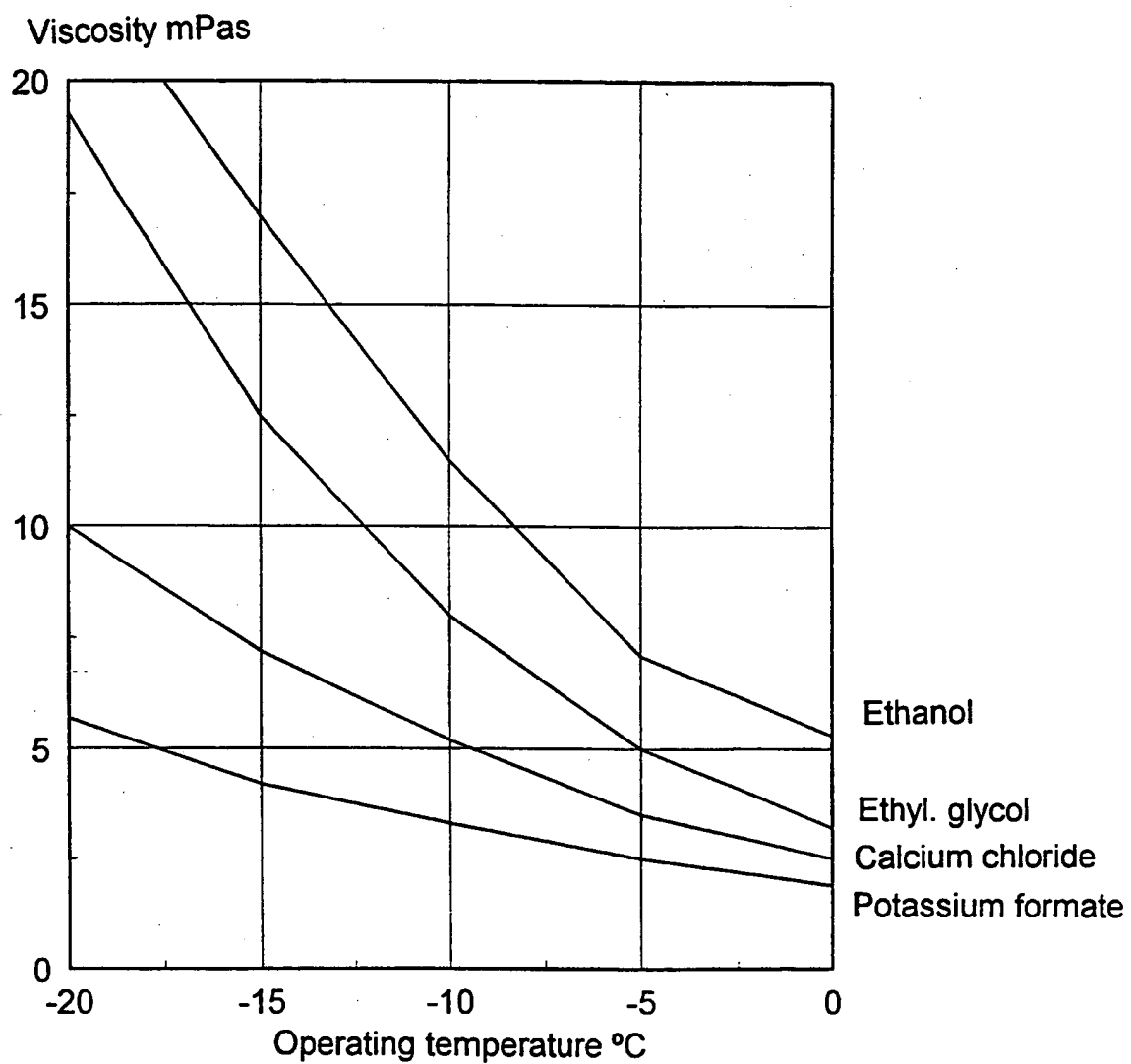


Fig. 1

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*Fig. 2*

*Fig. 3*

*Fig. 4*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00327

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 5/04, F25B 15/02

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K, F25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9309198 A1 (ATKINSON, STEPHEN), 13 May 1993 (13.05.93), page 2, line 4 - line 5; page 11, line 12 - line 24; page 13, line 5 - line 14, figure 3 --	1-4,6-12, 14-18
A	US 5104562 A (PETER KARDOS ET AL), 14 April 1992 (14.04.92), abstract --	1-18
A,P	EP 0677563 A1 (LINDE AKTIENGESELLSCHAFT), 18 October 1995 (18.10.95), abstract -- -----	1-18

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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